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NO DRAWINGS

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The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act, 1949 are:— WILLY BRAUN and ROLF MECKE, citizens of the Federal Republic of Germany, residing, respectively, at 11 In der unteren Rombach, Heidelberg; and 16 Ungsteiner Strasse, Ludwigshafen/Rhein; Federal Republic of Germany.

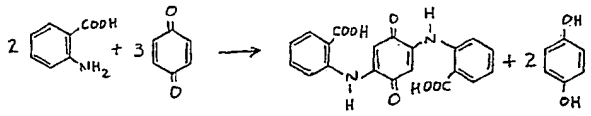
COMPLETE SPECIFICATION

Production of 2,5-Bis-(o-Carboxyarylamino)-1,4-Benzoquinones

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

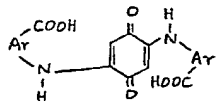
This invention relates to a new and advantageous process for the production of 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones. These dicarboxylic acids may be used for example for the production of linear-trans-quinacridonequinones.

It is known (vide J.C.S. 1955, pages 4440—4443) that 2,5-bis-(o-carboxyanilino)-1,4-benzoquinones can be obtained by reacting anthranilic acids with 1,4-benzoquinone. This method of production, which proceeds according to the following equation:



has the disadvantage that 3 moles of benzoquinone are required to two moles of anthranilic acid, and 2 moles are lost as hydroquinone.

We have now found that 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones having the general formula:



I

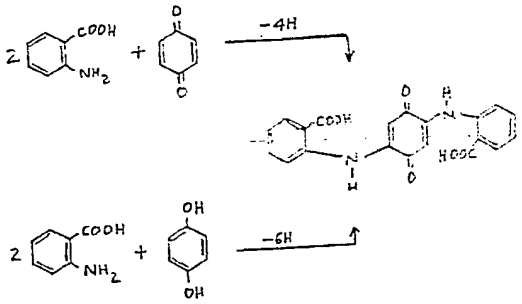
in which the two radicals Ar are identical aromatic radicals, are obtained particularly advantageously by allowing an oxidizing agent to act in a solvent on an o-carboxyarylamine having the general formula II:

II

[*Price 4s. 6d.*]

in which Ar has the above meaning, in the presence of benzoquinone or hydroquinone.

In the simple case in which the radical Ar in the formulae I and II denotes a benzene radical, the reaction according to this invention proceeds as follows, depending on whether benzoquinone or hydroquinone is used:



Thus only one mole of benzoquinone or one mole of hydroquinone is required for two moles of anthranilic acid.

The compounds having the general formula II to be used for the process according to the invention are anthranilic acids which may bear on the benzene nucleus one or more monovalent radicals and/or attached carbocyclic or heterocyclic rings. Examples of monovalent radicals are: halogen atoms, such as fluorine, chlorine, bromine or iodine atoms, alkyl groups, such as low molecular weight alkyl groups, aryl groups, such as phenyl or naphthyl groups, alkoxy groups, aryloxy groups, hydroxyl groups, nitro groups, amino groups, acylamino groups, sulfonic amide groups or trifluoromethyl groups. Examples of attached carbocyclic or heterocyclic rings are those which, with the benzene ring of the anthranilic acid, give the ring system of naphthalene, anthracene, carbazole, diphenylene oxide or diphenyl sulfide. The following may be given as examples of such substituted anthranilic acids: 3-chloroanthranilic acid, 4-chloroanthranilic acid, 5- chloroanthranilic acid, 3-methyleneanthranilic acid, 4-methyleneanthranilic acid, 5-methyleneanthranilic acid, 3-aminonaphthalene-2-carboxylic acid and 1-aminonaphthalene-2-carboxylic acid.

Oxidizing agents which will oxidize hydroquinones to quinones are suitable for the process of this invention. For example oxidizing agents which are conventionally used for the oxidation of hydroquinones to quinones may be used, such as potassium iron (III) cyanide, iron(III) chloride, hydrogen peroxide, atmospheric oxygen, sodium persulfate, potassium persulfate, ammonium persulfate, sodium bromate, potassium bromate and preferably sodium chlorate or potassium chlorate. The oxidizing agent is advantageously used in stoichiometric or larger amounts.

Reaction of benzoquinone or hydroquinone with the said anthranilic acids and the said oxidizing agents is carried out in a solvent. Suitable solvents are water, organic solvents which are miscible with water, such as methanol, ethanol, acetone or preferably mixtures consisting of water and an organic solvent miscible with water. In some cases it is advantageous to add one of the conventional oxygen transferrers, for example a vanadium salt, vanadium pentoxide or a molybdenum salt, in small amounts to the reaction mixture to accelerate the reaction.

Reaction to form the 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones generally proceeds with spontaneous heating up. It is therefore advantageous to keep the temperature of the reaction mixture at about 20° to 60° C. by occasional cooling, 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones separate during the course of the reaction in crystalline form and may be isolated by simple filtration.

2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones obtainable according to this invention are valuable intermediates, for example for the production of dyes. They are particularly suitable for the production of linear-trans-quinacridonequinones. Cyclization to the linear-trans-quinacridonequinones may be achieved for example by treating the 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones with dehydrating agents, for example by heating them in concentrated sulfuric acid or in polyphosphoric acid at about 80° to 200° C. 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones may also be converted with halogenating agents, such as thionyl chloride, phosphorus pentachloride or phosgene, into the acid halides and cyclization of these to linear-trans-quinacridonequinones effected by heating, advantageously in an organic solvent or diluent. Examples of suitable solvents and diluents are benzene, halobenzenes or nitrobenzene. It is not

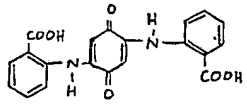
necessary to isolate the acid halides. Rather the 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones may be converted in one of the said solvents or diluents with one of the said halogenating agents into the acid chlorides by heating to about 30° to 80° C. and then cyclization may be brought about by further heating, for example at 60° to 200° C.

It is known that anthranilic acids are very susceptible to oxidation and that by the action of oxidizing agents on solutions of these acids, undefined tarry compounds form very readily. It is therefore surprising that 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones may be prepared in good yields and in good purity by the process according to this invention.

The invention is further illustrated by the following Examples. The parts and percentages specified in the examples are by weight.

EXAMPLE 1.

11 parts of benzoquinone, 30 parts of anthranilic acid and 0.5 part of vanadium pentoxide are heated to 45° C. in 250 parts of 60% aqueous methanol. A solution of 10 parts of sodium chlorate in 30 parts of water is added thereto during the course of half an hour. Then the whole is stirred for another five hours at 40° to 50° C. The residue is filtered off, washed with methanol and water and dried. 34 parts of 2,5-bis-(o-carboxyanilino)-1,4-benzoquinone having the constitution:



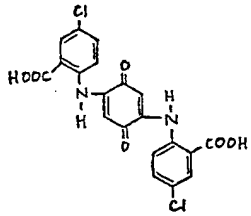
is obtained in the form of red needles.

EXAMPLE 2.

11 parts of hydroquinone and 30 parts of anthranilic acid are dissolved in 250 parts of 60% aqueous methanol. 0.1 part of ammonium metavanadate is added and then during the course of half an hour, a solution of 13 parts of sodium chlorate in 30 parts of water is dripped in. The temperature is kept at 40° to 45° C. by cooling. The whole is then stirred at the same temperature for another four hours. The residue is filtered off and washed with methanol and water. 34 parts of 2,5-bis-(o-carboxy-anilino)-1,4-benzoquinone is obtained in the form of red brown needles.

EXAMPLE 3.

The anthranilic acid in Example 1 is replaced by an equivalent amount of 4-chloroanthranilic acid. 2,5-bis-(2-carboxy-4-chloroanilino)-1,4-benzoquinone having the constitution:



is obtained. By cyclization in concentrated sulfuric acid it yields 2,9-dichloro-linear-trans-quinacridonequinone.

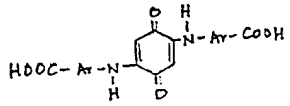
EXAMPLE 4.

11 Parts of hydroquinone and 30 parts of anthranilic acid are heated at 50° C. in a mixture of 300 parts of ethanol and 100 parts of water. A suspension of 80 parts of potassium peroxide disulfate in 200 parts of water is added thereto during the course of half an hour. The whole is then stirred for another five hours at 50° C. The product is suction filtered, washed with ethanol and hot water, and dried. 33 parts of 2,5-bis-(o-carboxyanilino)-1,4-benzoquinone is obtained. It may be cyclized in concentrated sulfuric acid to give linear-trans-quinacridonequinone.

If the suspension of potassium persulfate in water be replaced by a solution of 100 parts of iron(III) chloride in 200 parts of water and the above procedure is otherwise followed, the same product is obtained.

WHAT WE CLAIM IS:—

1. A process for the production of 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones having the general formula:



in which the two radicals Ar denote the same aromatic radical wherein an oxidizing agent is allowed to act in a solvent on an o-carboxyarylamine having the general formula HOOC—Ar—NH_2 in which Ar has the above meaning in the presence of benzoquinone or hydroquinone.

2. A process as claimed in claim 1 wherein the o-carboxyarylamine is anthranilic acid or an anthranilic acid bearing one or more chlorine atoms or methyl groups in 3-, 4- or 5-position.

3. A process as claimed in claim 1 or 2 wherein the reaction is carried out in water.

4. A process as claimed in claim 1 or 2 wherein the reaction is carried out in a water-miscible organic solvent.

5. A process as claimed in any of claims 1 to 4 wherein the reaction is carried out in a mixture of water and a water-miscible organic solvent.

6. A process as claimed in any of claims 1 to 5 wherein a conventional oxygen transferrer is added in a small amount.

7. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

8. 2,5-bis-(o-carboxyarylamino)-1,4-benzoquinones when obtained by the process claimed in any of claims 1 to 7.

9. A process as claimed in any of claims 1 to 7 wherein the product is cyclized to form a linear-trans-quinacridonequinone.

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